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(54) A method of stripping a resist mask.

(57) In a downstream ashing apparatus for removing a used organic resist on a silicon semiconductor wafer, according to the present invention, water vapor is added into an oxygen plasma gas generated by a microwave power. The addition of the water vapor lowers an activation energy of the ashing reaction, and increases reactive species generated in the plasma, accordingly the ashing rate is increased even at as low as 150 °C of the wafer temperature. The addition of water vapor increases the ashing rate for a wide range of water content, such as from 5 to 80 %, allowing an easy control of the process. The lowered operating temperature prevents contamination of the semiconductor wafer. Nonuse of CF<sub>4</sub> protects the SiO<sub>2</sub> layer from being undesirably etched, resulting in prevention of deteriorating the semiconductor characteristics.

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## A METHOD OF STRIPPING A RESIST MASK

### BACKGROUND OF THE INVENTION

#### Description of the Related Art

This invention relates to an improvement of a method of stripping a resist mask (referred to hereinafter as ashing).

As well known, a mask made of an organic photoresist, etc., is necessarily employed in a photo lithography technique for fabricating semiconductor devices, etc.. After the photoresist is exposed to a light for the photo lithography, the resist must be removed. For removing this used photoresist, a plasma dry etching method, particularly a downstream ashing method, is widely employed. The downstream etching apparatus is such as disclosed by the present inventor in U.S. patent No. 4,512,868 and has been used for processing a silicon wafer, etc., where the wafer is protected from being bombarded by charged particles of the plasma.

The reaction gas used therein for ashing the organic photo resist is, for example, an oxygen gas including a  $\text{CF}_4$  (carbon tetra-fluoride) gas, etc.. However, it is not always easy to remove the used resist. This is because the resist having been affected by its exposure to a light at the exposure process and also its exposure to the plasma in a prior silicon etching process, etc., thus is hardened. Furthermore, the  $\text{CF}_4$  is apt to undesirably etch the silicon wafer. For improving the ashing rate, there is a method in which a nitrogen gas is added to the oxygen containing reaction gas to increase the number of the oxygen atoms, as reaction species. In this method containing 10 % nitrogen for example, the ashing rate is  $0.3 \mu\text{m}/\text{minute}$  at  $180^\circ\text{C}$ , and the increase of the ashing rate achieved with this method is still limited, because the reactive species are mainly the oxygen atoms only, and the function of the above added nitrogen gas is considered to increase only the number of the oxygen atoms as the reactive species. As another way for increasing the number of oxygen atoms, there is known a plasma etching method in which a small amount of water vapor is added to the oxygen plasma gas. However, no extensive study or application has been carried out, because its beneficial effects have not been appreciated.

### SUMMARY OF THE INVENTION

It is a general object of the invention, therefore to provide an improved ashing method for fast stripping a used resist off a semiconductor wafer.

It is another object of the invention, to lower the activation energy of the reaction, accordingly lowering the reaction temperature.

It is still another object of the invention, to prevent a deterioration of the semiconductor wafer caused by a contamination with metal components contained in the resist.

It is a further object of the invention, to avoid the use of  $\text{CF}_4$  so as to avoid an undesirable etching of silicon wafer during the resist stripping, accordingly to prevent lowering the withstanding voltage of the insulation.

According to the present invention, in a downstream etching apparatus a water vapor is added into an oxygen gas, a reaction gas. The amount of the added water vapor is preferably more than 1 per cent of the total reaction gas by the flow rate.

The addition of the water vapor into the oxygen gas increases reactive species, accordingly the ashing rate, at a wafer processing temperature as low as  $150^\circ\text{C}$ . The lowered ashing temperature prevents contamination of the semiconductor wafer with metal atoms.

The above-mentioned features and advantages of the present invention, together with other objects and advantages, which will become apparent, will be more fully described hereinafter, with reference being made to the accompanying drawings which form a part hereof, wherein like numerals refer to like parts throughout.

### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 shows effects of water addition in various reaction gases on activation energy.

FIG. 2 shows effects of water addition in an oxygen gas on ashing rate and on number of the atomic oxygen in oxygen plasma according to the present invention.

FIG. 3 shows effects of nitrogen addition in an oxygen gas on ashing rate and on number of the atomic oxygen in prior art gas plasma.

FIG. 4 shows a downstream ashing apparatus for embodying the present invention.

FIG. 5 shows another method for mixing the water vapor into the oxygen gas, for embodying the present invention.

# DESCRIPTION OF THE PREFERRED EMBODIMENTS

Referring FIG. 1 through FIG. 3, effects of embodying the present invention are presented. An apparatus used for obtaining the data of FIGs. 1 to 3 is schematically illustrated in FIG. 4. This apparatus is commonly used for a downstream ashing, where an microwave power, of typically 2.45 GHz, is fed through a wave guide 1 into a microwave cavity 2. A plasma generating chamber 8 is a part of the cavity 2 and is vacuum-sealed by a quartz plate 2' which is transparent for the microwave power. Reaction gases are fed respectively from outside sources 37 and 38 of oxygen and water, via valves 35 and 36, and flow meters 33 and 34 to the plasma generating chamber 8. Accordingly, a plasma of the reaction gases is generated in the plasma generating chamber 8. On a wall 4, opposite to the quartz plate 2', of the plasma generating chamber 8 there are provided many small holes 41 which connect the plasma generating chamber 8 to a reaction chamber 5 but shield the microwave power. The reaction gas including reactive species, such as oxygen atoms, generated in the plasma flow out of the plasma generating chamber 8 through the holes 41 into the reaction chamber 5 as shown by arrows in FIG. 4. In the reaction chamber 5, a semiconductor wafer 7 to be processed is placed on a stage 6 in a flow of the reaction gas from the holes 41, so that the reactive species reacts with the resist on the semiconductor wafer 7. Temperature of the stage 6 is raised and controlled by a heater 61 installed in the stage. The reaction gas in the reaction chamber 5 is evacuated by a pump (not shown in the figure) through an outlet 51.

As for the ashing process procedure, the wafer 7 on the stage is once heated up as high as approximately 200 °C while the chamber 5 is evacuated to approximately 0.01 Torr by the pump. Next, the inner pressure of the reaction chamber 5 is raised up to approximately 0.8 Torr and the approximately 1.5 kW microwave power is applied to the plasma generating chamber 8 so as to generate a gas plasma therein.

FIG. 1 shows effects of adding water, nitrogen or hydrogen to an oxygen gas, measured by their flow rate ratio, on activation energy. From FIG. 1 it is observed that the activation energy is lowered from approximately 0.5 eV to approximately 0.4 eV by adding hydrogen or water; however, no effect is observed by adding nitrogen. On the other hand, as well known, a speed constant  $k$  of a chemical reaction is generally given by the following formula named Arrhenius' equation:

$$k = A \exp(-E/RT)$$

where  $A$  indicates a frequency factor,  $E$  indicates an activation energy,  $R$  indicates a gas constant and  $T$  indicates the absolute temperature. Therefore, lowered value of the activation energy means a faster reaction at a certain temperature, in other word, a certain reaction speed achieved at a lower temperature.

Effects of adding water were observed by the inventors, and are shown in FIG. 2, for which a 1,000 cc/min reaction gas flow, including oxygen gas added with water vapor and 50 cc/min of argon gas are used in the apparatus shown in FIG. 4, keeping the wafer temperature at 180 °C. Percentage of the water vapor content,  $H_2O/(O_2 + H_2O)$ , is measured by their flow rate. The argon gas, which has no effect on the ashing reaction, is added thereto just for generating a standard light spectrum with which oxygen atoms, etc., can be quantitatively compared by a actinometry technique, which is as reported by J.W. Coburn et al. on Journal Applied Physics, vol. 51, No. 6, 1980. pp. 3134. A glass fiber 9 is installed on the wall of the cavity 2 to watch the lights generated in the plasma through the transparent quartz plate 7, which is also optically transparent. Another end of the glass fiber 9 is connected to a monochromator 10. In FIG. 2, black dots show the ashing rate scaled by the right hand side vertical axis, and white dots show the relative oxygen atom concentration scaled by the left hand side vertical axis. The relative oxygen atom concentration is measured by an actinometry method, i.e. by the ratio of the intensity of 8158 Å oxygen atom spectrum to the intensity of 7067 Å argon spectrum.

It is observed in FIG. 2 that an addition of approximately 10 % to 60 % of water vapor almost doubles the ashing rate of the case where no water is added, and the ashing rate completely relates to the amount of the oxygen atom concentration. However, at the range over 50 % of water content, the ashing rate curve slowly falls but the oxygen atom concentration curve falls faster than the ashing rate curve. This separation of the oxygen atom concentration curve from the ashing rate curve suggests that another reactive species, such as OH (hydroxide) radical, etc., are also contributing to the ashing reaction. For comparison, an effect of the nitrogen addition to an oxygen is shown in FIG. 3, for which the total gas flow and the temperature are the same as those of FIG. 2. In FIG. 3, the black and white dots respectively show the same as in FIG. 2, and the triangle dots show a relative concentration of the oxygen atoms measured by 4368 Å oxygen atom spectrum. In either of FIG. 2 and FIG. 3, the ashing rates are almost the same, i.e. 0.3 μm/minutes, at 180 °C. However, as the effect of the lowered activation energy, the ashing rate of 40 % water-containing oxygen achieves

0.15  $\mu\text{m}/\text{minute}$  is achieved at as low as 150 °C, compared with 0.1  $\mu\text{m}/\text{minute}$  of an 10 % nitrogen-containing oxygen which is optimum for the fastest ashing rate, at the same temperature. These data are not shown in a figure. The lowered temperature for the ashing is significantly advantageous in that the semiconductor wafer is protected from a contamination of the metal components included in the resist material. As well known, the metal contamination deteriorates the semiconductor properties, such as heavy metals lower the minority carrier generation life time, and alkaline metals also contaminate the semiconductors.

As seen in FIG. 2, the curve of the ashing rate of the water-containing oxygen is relatively flat over the wide range of the water content, i.e. from 10 % to 80 % approximately, and is much wider than the range 5 to 15 % of the nitrogen-containing oxygen as shown in FIG. 3. This is advantageous for an easy control of an ashing operation at a production stage.

The beneficial advantage of avoiding the use of  $\text{CF}_4$  is as follows. When a 10 %  $\text{CF}_4$ -containing oxygen gas is used for the resist etching in a downstream apparatus, the  $\text{SiO}_2$  layer on the semiconductor wafer is also etched undesirably. The ratio of the resist ashing rate to the  $\text{SiO}_2$  etching rate, i.e. the selectivity, is typically 300 to 500. That is to say, while 1  $\mu\text{m}$  of the resist is ashed, the  $\text{SiO}_2$  is etched 30 Å, for example. This undesirable etching of the underlying  $\text{SiO}_2$  layer used for a gate insulation lowers the withstanding voltage of the gate insulation, or deteriorates electrical characteristics of the semiconductor circuits. There is the same problem with polycrystalline silicon, SiN, or aluminum, as well. This problem has not been so serious in fabrication of conventional relatively low-density LSI (large scale integrated circuit), because the insulation layer is as thick as 1000 Å for 16 K bit memory devices. However, this problem is now becoming serious for fabricating the most up-to-date 1 M bit memory devices, because the insulation layer is as thin as 200 Å or less. According to the method of the present invention, there is no longer the undesirable etching problem of the  $\text{SiO}_2$  layer, etc., at all.

As described above, in the downstream ashing apparatus the gas plasma, i.e. the electromagnetic power to generate the plasma, is confined in the plasma generating chamber by a shielding wall, only the reactive species generated in the plasma come out via many small holes on the shielding wall. The holes shield the electromagnetic waves but allow the reactive species to pass therethrough to react with the resist material. Therefore, the wafer is protected from a bombardment of the charged particles, such as ions, which may cause the deterioration of the semiconductor materials.

Therefore, the reaction is purely chemical. The above-described beneficial effects of adding the water vapor in an oxygen gas can be significantly enhanced by being combined with the beneficial effect of the downstream apparatus, and is highly appreciated in the production of VLSI (very large scale integrated circuit) such as of submicron integration.

Typical and preferable methods of adding the water vapor to the oxygen gas are schematically illustrated in FIG. 4 and 5, where the same or equivalent parts are denoted with the same numbers of those of FIG. 4. In the apparatus of FIG. 4, the plasma generating chamber 8 is provided with two gas inlets 31 and 32, for introducing oxygen gas and water vapor respectively and independently from each other. Each gas is supplied to the inlet 31 and 32 from each gas source 37 and 38 through a control valves 35 and 36 and flow meters 33 and 34, respectively. If the gases are to be fed into the plasma generating chamber 8 through a single inlet, the amount of mixing the water vapor into the oxygen gas is influenced by the amount of the oxygen gas flow and the fluid resistance of the inlet pipe between the place of the water vapor mixing to the chamber 8. Therefore, in such an apparatus, it is not easy to control to add a large amount of the water vapor, such as more than 10 %, because of the relatively high gas pressure of the oxygen gas caused by the above mentioned fluid resistance. However, this problem can be solved in the apparatus shown in FIG. 4.

In the apparatus of FIG. 5, the water vapor is mixed into the oxygen flow while the oxygen gas is flowing, in other words, bubbling through a heated water 39 on the way from the gas source 37 to the chamber 8. The amount of the added water vapor is determined by the balance of the vapor pressure of the water 39 at its present temperature and the pressure of the oxygen. The water vapor pressure can be raised and controlled by the temperature of the water through which the oxygen gas is flowing. The water temperature is controlled by the heater 40. Because of relatively high vapor pressure of the heated water, a considerable amount, such as more than 10 %, of the water vapor can be easily mixed into the oxygen gas, under precise control.

As shown in FIG. 1 an addition of a hydrogen gas into an oxygen gas exhibits a good effect to lower the activation energy. However, as is well known, the mixture of more than 3 % hydrogen gas in the oxygen gas will cause an explosion. Therefore, the hydrogen gas can not be industrially employed as the plasma reaction gas.

The many features and advantages of the invention are apparent from the detailed specification and thus, it is intended by the appended claims to cover all such features and advantages of the

method which fall within the true spirit and scope of the invention. Further, since numerous modifications and changes may readily occur to those skilled in the art, it is not desired to limit the invention to the exact construction and operation shown and described, and accordingly, all suitable modifications and equivalents may be resorted to, falling within the scope of the invention.

## Claims

1. An ashing method for removing a used organic resist from a semiconductor wafer, comprising:

generating a gas plasma of an oxygen gas containing water vapor by applying an electromagnetic power to a plasma generating chamber; and introducing reactive species generated in said gas plasma from said plasma generating chamber via holes of a chamber wall toward the semiconductor wafer to react with the used organic resist; said wall and said holes essentially shielding said semiconductor wafer from said electromagnetic power.

2. An ashing method for removing a used organic resist according to claim 1, wherein the contents of said water vapor is more than 1 % of the total gas by flow rate.

3. An ashing method for removing a used organic resist according to claim 1 or 2, wherein said electromagnetic power is a microwave power.

4. An ashing method for removing a used organic resist according to claim 3, where said microwave power is of essentially 2,45 MHz.

5. A plasma ashing apparatus for removing a used organic resist on an semiconductor wafer, comprising:

a plasma generation chamber (8) for generating a plasma of a reaction gas including an oxygen gas and a water vapor, said plasma being generated by an excitation of an electromagnetic power applied into said plasma generation chamber;

a first gas inlet (31), operatively connected to said plasma generating chamber, for feeding other part of said reaction gas than said water vapor into said plasma generating chamber;

a second gas inlet (32), operatively connected to said plasma generating chamber, for feeding said water vapor into said plasma generating chamber;

a flow control means (36) for regulating a flow of said water vapor into said plasma generating chamber;

a reaction chamber (5) for placing a semiconductor wafer (7) therein, said reaction chamber being separated by a wall (2') from said plasma generating chamber, said wall having holes (41) on said wall for supplying a reactive species generated in said plasma into said reaction chamber, said holes es-

entially shield said semiconductor wafer from said electromagnetic power, whereby said reactive species reacts with the used organic resist to be removed; and

a gas outlet (51) operatively connected to said reaction chamber for evacuating said reaction chamber.

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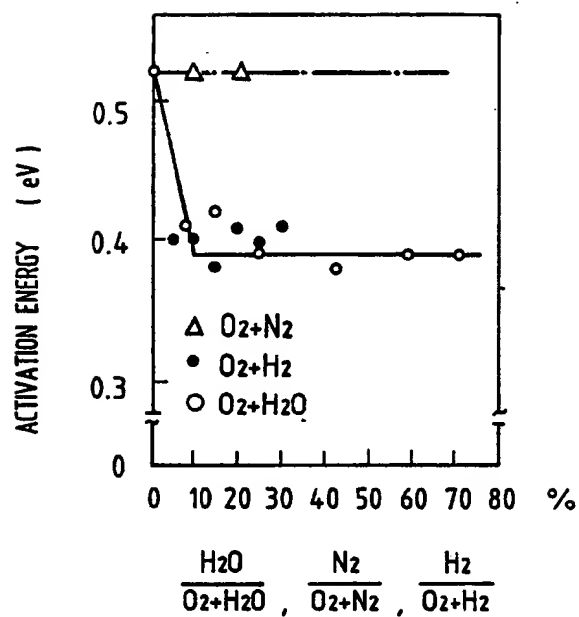


FIG. 1

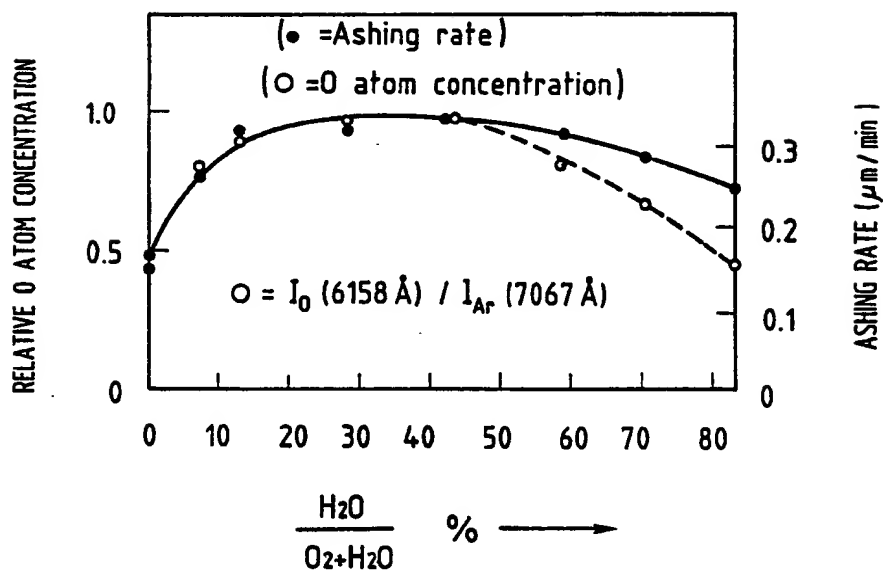


FIG. 2

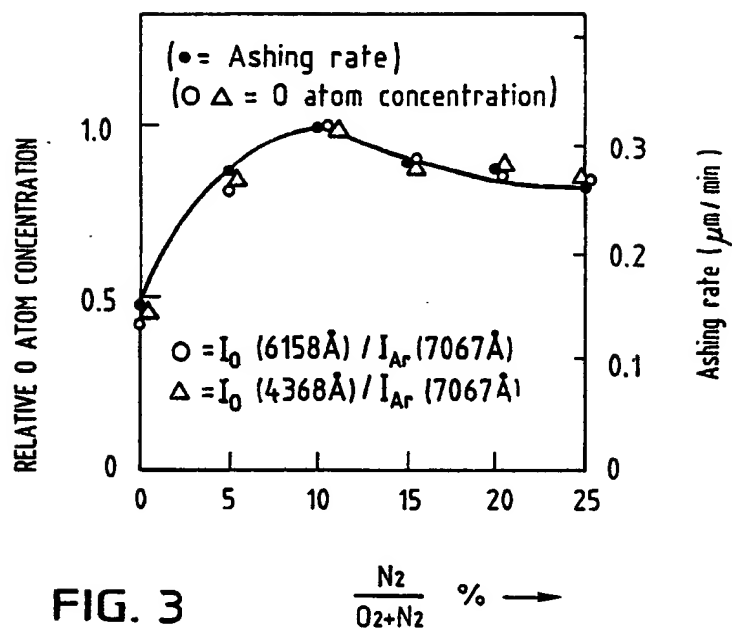


FIG. 3

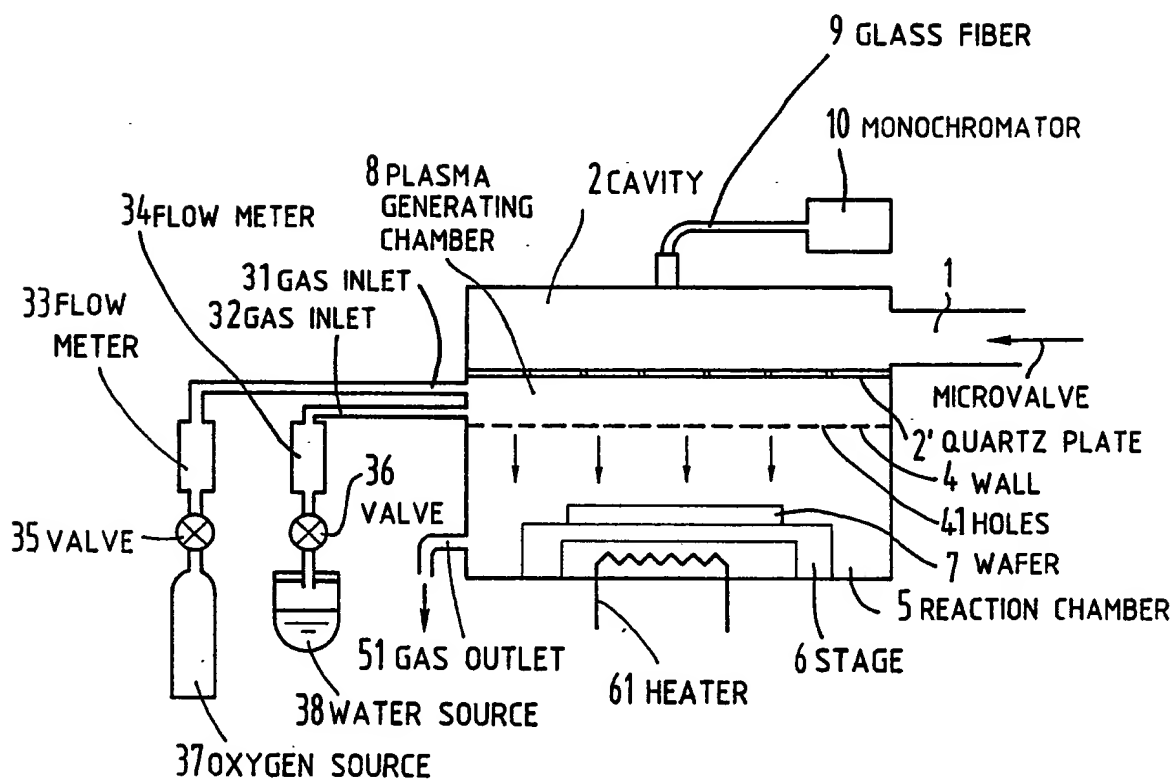


FIG. 4

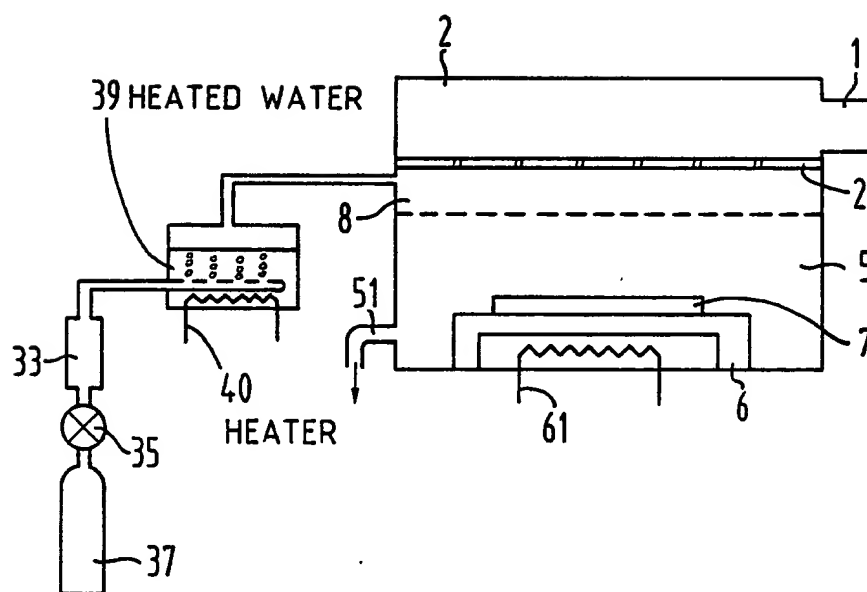


FIG. 5